PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PRODUCTION OF COLOURED ANODIC OXIDE COATINGS

(71) We, RIKEN KEIKINZOKU KOGYO KABUSHIKI KAISHA, a Japanese body corporate of 3—2—1 Magarikane, Shizuokashi, Shizuoka-ken, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of producing coloured anodic oxide coatings on aluminium or aluminium based alloy materials.

It has been proposed hitherto to produce coloured anodic oxide films on aluminium or aluminium alloys (hereinafter simply referred to as aluminium-based materials) by firstly anodizing the aluminium-based materials to produce anodically oxidized films thereon, and then subjecting them to an electrolytic process wherein the anodized materials are dipped in a bath of an electrolyte having a metal salt dissolved therein so that the metal serves as one or both of the electrodes. As a result, anodic oxide films are applied to the materials with colours which can differ in accordance with the metal salts added to the bath.

For example, the United States Patent Specification 3,382,160 describes the colouring of anodic oxide films on aluminium-based metals by subjecting the anodized aluminium-based metals to an electrolytic process with alternating current in an acidic bath containing metal ions such as nickel, cobalt, chromium, copper or cadmium ions. Further, United States Patent Specification 3,669,856 describes the easy control of the colour of anodized films by subjecting anodized metals to asymmetric alternating voltages in an anodic bath containing metal ions.

In these electrolytic colouring processes, the anodic oxide films are coloured by the metal ions which are first drawn into the pore structure of the anodic oxide films in an operation cycle wherein the metal is subjected to a negative voltage, and then removed when the metal is subjected to a positive voltage. The colours thus produced on the anodic oxide films will depend on the locations and the amounts of metal ions removed from the pore structures of the films. However, the hitherto proposed processes cannot provide positive control of such locations and the amount of metal ions in the pore structures of the films. Control is instead performed by selecting the bath temperature and processing time so as to obtain a desired amount of removal of metal ions. It is therefore very difficult to obtain products of uniform colour. In hitherto proposed processes, it has been experienced that even very small variations in processing time influence the colours produced in the films.

For example, referring to bronze-based colours, which include bright amber as well as dark-blackish colours, it has been very difficult to obtain products of a desired and uniform colour using the hitherto proposed processes since colour changes have been experienced even in the same production lot, due to very small unavoidable changes in the bath temperature and the processing time.

According to the present invention there is provided a method for producing coloured anodic oxide films comprising the steps of subjecting an aluminium based material to an anodizing treatment to produce an oxide film thereon, dipping the previously anodized material in a bath of electrolyte containing from 15 to 150 grams of water-soluble nickel salt per litre of water and from 10 to 50 grams of boric acid per litre of water, and applying to the material voltage pulses of opposite polarity, the time integral of the applied negative voltage being greater than the time integral of the applied positive voltage.

Since, in accordance with the present

invention, the electrolyte contains boric acid, a complex of the nickel salt and boric acid is formed in the vicinity of a previously-formed anodic film. Further, the aluminium-based material is subjected to high energy levels at the rising and end periods of each pulse. Thus, the colouring agents or the metal ions rapidly fill active sites in the porous structure of the anodic oxide films, so that removal of the colouring metal ions is terminated after a predetermined time to produce uniform and identical colours.

Preferred embodiments of process in accordance with the present invention will now be described.

An aluminium-based material is first subjected to a conventional anodizing treatment to produce an oxide film thereon. The anodized material is then dipped into a bath of an electrolyte containing boric acid and a water-soluble nickel salt so that it constitutes an electrode. The other, opposing electrode can consist of another anodized material. The bath includes 10 to 50g of boric acid for each litre of water. Boric acid is preferably added until the electrolyte is saturated therewith. The amount of water-soluble nickel salt is 15 to 150 grams per litre of water. It is preferable that nickel acetate, nickel sulphate or nickel chloride be used as the water-soluble nickel salt, however, other nickel salts can be used if they are soluble in water.

Voltage pulses, of opposite polarities, with the duration of the negative pulses being equal to or greater than that of the positive pulses, are applied to the aluminium-based material dipped in the electrolyte. The voltage applied to the material being treated can comprise alternating positive and negative pulses or it can comprise a plurality of positive pulses followed by a plurality of negative pulses. Pulsating voltages of any wave form can be applied, provided they can apply high energy levels to the materials to be treated.

The anodic oxide film on the material is provided with a bronze colour, which is inherent to nickel ions, and which can be selected in a range from bright amber to dark blackish colours, simply by controlling the values of the alternating voltage pulses. It is possible to provide uniform and substantially identical colours to anodic oxide films, provided the treatment is performed beyond a certain duration. No colour changes have been found with changes in processing time and/or temperature.

The following Example is given by way of illustration only.

Example.

An aluminium alloy A.A. 1100 was first subjected to a conventional anodizing process to form an oxide film thereon. The material was then dipped in a bath of a colouring electrolyte containing 50g of boric acid and 100g of $(CH_3COO)_2.Ni4H_2O$ per litre of water. Thereafter, a colouring electrolytic process was performed by applying alternating positive and negative voltage pulses to the material for 3 to 10 minutes. The bath was maintained at a temperature for 20 to 22°C. The results are shown in Table 1, wherein the characters X, Y and Z designate Munsell notations.

From Table I, it will be understood that an amberlike colour can be produced by applying alternating voltage pulses to the material, the pulses consisting of alternating negative voltage pulses of 13 volts for 3 seconds duration and positive voltage pulses of 13 volts for 1 second duration. The treatment was performed for at least 7 minutes. The processing time did not have any effect on the colour produced.

The composition of the bath was determined in accordance with the following experiment.

Aluminium-based materials having anodic oxide films thereon were dipped in a bath of an electrolyte having one of the compositions shown in Table 2, and they were maintained at a temperature of 20 to 22°C. Alternating voltage pulses were then applied between the materials for five minutes. The alternating voltage pulses consisted of negative pulses of 12.5 volts average and 3 seconds duration, and positive pulses of 5.5 volts average and 1 second duration. The results obtained are also shown in Table 2. The Munsell notations in Table 2 are averages from several experiments. Since visual tests showed that variations in colour were the smallest with the bath containing 100 g/l of nickel salt and 50 g/l of boric acid, an electrolyte of this composition was used.

Using a process embodying the present invention, it is possible to produce coloured anodic oxide films on aluminium-based materials with minimum variations in colour. Colours can also be produced in anodic oxide films on aluminium-based materials in a bath of electrolyte having a pre-selected composition.

TABLE 1

Processing Data						Colour Tone		
Negative Pulse		Positive Pulse						
Average Potential (Volts)	Duration (sec)	Average Potential (Volts)	Duration (sec)	Processing Time (min)	Colour	Y	X	Z
13	3	13	1	3	Amber	29.95	29.40	24.38
				5		22.65	22.25	17.90
				7		14.20	14.35	10.35
				10		15.20	15.03	10.15
13	3	10	3	3	Rich Amber	29.00	28.23	22.20
				5		19.03	18.65	14.07
				7		15.85	15.65	11.52
				10		14.90	14.55	10.33
13	3	11	1	3	Bronze	15.12	14.88	10.53
				5		9.74	9.58	6.73
				7		5.11	4.72	3.75
				10		4.75	4.23	4.42
15	3	13	1	3	Rich Bronze	14.82	14.76	10.53
				5		7.75	7.35	6.10
				7		4.80	4.43	3.92
				10		4.56	3.96	4.48
15	3	10	1	3	Black	7.85	7.56	5.80
				5		5.45	5.03	4.90
				7		4.82	4.42	4.90
				10		4.32	3.63	4.65

TABLE 2

Electrolyte (g/l)		Colour Tone		
Ni Salt	Boric Acid	Y	X	Z
10	20	4.4	3.7	4.4
	35	3.5	2.8	3.8
	50	3.3	2.9	3.6
20	20	3.0	2.3	3.6
	35	2.7	2.2	3.3
	50	2.5	2.0	3.0
30	20	2.7	2.1	3.4
	35	2.6	2.1	3.3
	50	2.2	1.7	2.8
40	20	2.5	2.0	3.4
	35	2.7	2.1	3.5
	50	2.2	1.7	3.0
70	20	2.7	2.1	3.5
	35	2.5	1.9	3.2
	50	2.2	1.7	2.9
100	20	2.8	2.3	3.5
	35	2.2	1.8	2.8
	50	2.2	1.7	2.9

WHAT WE CLAIM IS:—

1. A method for producing coloured anodic oxide films comprising the steps of subjecting an aluminium based material to an anodizing treatment to produce an oxide film thereon, dipping the previously anodized material in a bath of electrolyte containing from 15 to 150 grams of water-soluble nickel salt per litre of water and from 10 to 50 grams of boric acid per litre of water, and applying to the material voltage pulses of opposite polarity, the time integral of the applied negative voltage being greater than the time integral of the applied positive voltage.

2. A method in accordance with claim 1, in which the negative and positive voltage pulses are applied alternately.

3. A method in accordance with claim 1 in which more than one negative pulse and thereafter more than one positive pulse is applied to the material in an alternating manner.

4. A method according to any of preceding claims wherein the average voltage of each negative voltage pulse is greater than that of each positive voltage pulse and duration of the negative pulses is equal to or greater than the duration of the positive pulses.

5. A method according to any of claims 1 to 3, wherein the average voltages of each negative voltage pulse and each positive voltage pulse are equal and the duration of

the negative voltage pulses is greater than that of the positive voltage pulses.

6. A method in accordance with claim 1, in which the water-soluble nickel salt is nickel acetate, nickel sulphate or nickel chloride.

7. A method in accordance with claim 1, substantially as herein described.

8. A method of producing a coloured anodic film on an aluminium-based material, the method being substantially as herein described with reference to the Example.

9. An aluminium based material having a coloured anodic film thereon, the film having been produced by a method in accordance with any of the preceding claims.

MATHISEN, MACARA & CO.,
Chartered Patent Agents,
Lyon House,
Lyon Road,
Harrow,
Middlesex HA1 2ET.
Agents for the Applicants.

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